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Separation and Recovery of Dimethylnaphthalene Isomers from Light Cycle Oil by Distillation-Extraction Combination

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ABSTRACT

Light cycle oil (LCO) contains a lot of valuable aromatic components, including 2,6-dimethylnaphthalene (2,6-DMNA) that is focused as the elementary raw material for engineering plastic (PEN plastic) and polymer liquid crystal. We investigated the separation and recovery of dimethylnaphthalene (DMNA) isomers by distillation-extraction combination as the pretreatment operation to separate and purify 2,6-DMNA from LCO. The concentration of DMNA isomers from LCO was tested by batch distillation operation. Distillate with DMNA isomers of high concentration, such as 30.63 wt%, was recovered by mixing distillates

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distilled at 255 to 278°C. Furthermore, equilibrium extraction to investigate separation between DMNA isomers and paraffin components in the distillate was carried out using the mixture oil added a small quantity of n-decane (DEC) to the distillate recovered through batch distillation operation as raw material and the aqueous N,N-dimethylforamide as a solvent. Selectivity of DMNA isomers in reference to DEC increased by increasing the solvent moisture and the mass ratio of solvent to raw material, whereas, selectivity of DMNA isomers in reference to DEC decreased by increasing the operation temperature. The process of separation and recovery for DMNA isomers from LCO was studied by using the experimental results obtained from each operation (distillation, extraction) of this work.

Key Words: Dimethylnaphthalene; Distillation; Light cycle oil; Solvent extraction; Recovery process.

INTRODUCTION

Recently, it is stressed that petroleum is used as a raw materials rather than energy in view of efficient resource utilization. Light cycle oil (LCO), which is one of by-products of the manufacturing process for catalytic cracking gasoline, contains a lot of valuable aromatic components, such as 2,6-dimethylnaphthalene (2,6-DMNA). 2,6-DMNA is paid attention to as a raw material for engineering plastic (PEN plastic) and polymer liquid crystal. Up to now, LCO mixed with heavy oil is used only as a fuel. Therefore, separation and purification of 2,6-DMNA from LCO is very significant in view of efficient resource utilization.

Concentrations of ten DMNA isomers (DMNAs) and 2,6-DMNA in LCO are about 9 wt% and 1 wt%, respectively. As Table 1 shows, the boiling points of each DMNA are very close, and it is difficult to separate each DMNA by distillation. Therefore, it is believed that multistage processes should be required to separate and purify of 2,6-DMNA from LCO; DMNAs in LCO were separated and recovered by an operation, such as distillation and organic solvent extraction,[1,2] and then 2,6-DMNA in DMNAs was purified by an operation such as High pressure crystallization,[3–6] adsorption,[7,8] and cooling crystallization.[3–5,9]

An extraction method using solvent, such as sulfolane, dimethylsulfoxide, diethylene glycol, triethylene glycol, tetraethylene glycol and ethylene carbonate, was widely used for dearomatizing petroleum products with lower boiling points, such as naphtha reformate and gasoline.[10–25] When LCO, a petroleum product with a higher boiling point, is dearomatized by the above-mentioned extraction solvent, it is difficult to

Table 1. Boiling points of each DMNA isomer.

Component	Boiling point (°C)
2,6-DMNA	262.0
2,7-DMNA	262.3
1,7-DMNA	262.7
1,3-DMNA	264.8
1,6-DMNA	265.7
1,4-DMNA	265.0
2,3-DMNA	269.2
1,5-DMNA	269.1
1,2-DMNA	271.4
1,8-DMNA	270.0

recover the solvent after the extraction operation because the boiling point between the extraction component and the solvent overlaps. Therefore, a re-extraction operation is required to separate the extraction components in the solvent phase, and the process for separation and recovery of DMNAs from LCO becomes very complicated.[1,2,25]

Benham et al.,[25] reported the dearomatization of LCO by a solvent extraction. They used a mixture of furfural and water as an extraction solvent to dearomatize LCO, and a mixture of xylene and naphtha as a re-extraction solvent to recover the extract components in the extract phase, i.e., redex process. This process mainly was for improving the cetane number of a raffinate oil and, subsequently, the experimental review on separating and recovering valuable bicyclic components, such as DMNAs in LCO, by extraction and re-extraction was found to be unsatisfactory.

In a previous work,[1,2] we investigated the recovery process of DMNAs in LCO by DMSO extraction-distillation combination as the pre-treatment operation for the separation and purification of 2,6-DMNA from LCO. The recovery process of DMNAs from LCO, which were composed of the extraction column for aromatic group in LCO, the re-extraction column for aromatic group in extract phase, and the distillation towers for recovery of DMNAs in aromatic group mixture, was complicated.

In this work, to avoid the complexity of a process using a re-extraction operation, the recovery of DMNAs from LCO were investigated with distillation-extraction combination as the pretreatment operation for the separation and purification of 2,6-DMNA from LCO. The concentration of DMNAs from LCO was tested by batch distillation operation, and then the separation between the paraffin components and the aromatic components in the distillate recovered through distillation operation was investigated with the equilibrium extraction. Aqueous DMF was used as a solvent, because of the significant difference of boiling points between distillate and solvent. Finally, the process for the recovery of DMNAs from LCO was studied by using the experimental results obtained from each operation (distillation and extraction) of this work.

EXPERIMENTAL APPARATUS AND METHOD

Distillation

The batch distillation apparatus used in this work is shown in Figure 1. The distillation column was made of Pyrex glass and its inner diameter and height were 5 cm by 0.7 m, respectively. One mm of Raschig rings filled in the column. The still (500 mL of Pyrex glass flask) was heated with a mantle heater (heating rate: 1°C/min) and its exterior was insulated with a ribbon heater and glass wool to prevent loss of heat through the distillation column. Steam temperature from the top was measured by copper-constantan placed in the center of the column. Also, 10°C of condensation temperature was uniformly maintained by recycling the cooling water. Reflux ratio was controlled by rotating the cooling pipe of the condenser.

LCO (400 mL) was heated in the still. After a steady state was reached, the reflux ratio was controlled. The reflux ratio was derived from the ratio

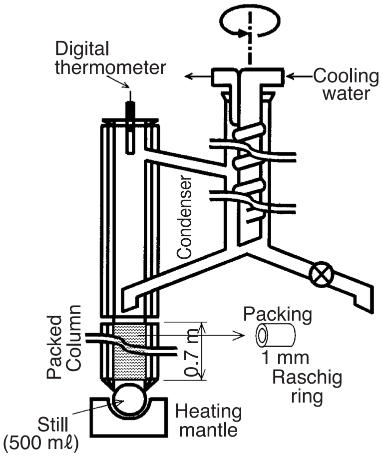


Figure 1. Details of batch distillation apparatus.

of drop numbers of the reflux liquid to that of the distillate. The distillate with 0.05 of distilled ratio (V_f = distillate volume/raw material volume) was recovered in another. The steam temperatures immediately after the recovery of each distillate were regarded as the distilled temperatures. Also, because a distillate more than $V_f = 0.9$ did not contain any DMNA, a distillate less than $V_f = 0.85$ was recovered. The operating pressure was 760 mm Hg. We assumed that the pressure had nothing to do with the temperature in the distillation column.

To analyze the distillate, acetone was added into each distillate recovered from the distillation. They were analyzed by a gas chromatograph (Hewlett Packard Co., HP6890: capillary column HP-1) equipped with a FID (flame ionization detector) and the composition of each distillate was determined.

Extraction

It was difficult to quantify the paraffin components (carbon number 13–17) that were possibly included in the distillate because of the peak of the aromatic components, which overlapped with that of the paraffin components in the gas chromatogram.[1,2] Therefore, in this work, 1.2 wt% of n-decane (DEC) was added into the distillate and aqueous DMF were used as raw material and solvent due to the significant difference of boiling points between them, respectively. The separation between DEC and the aromatic components in a raw material was investigated. From these results, we estimated the separation between the paraffin components and the aromatic components in the distillate.

First, DMF was mixed with city water to make a solvent of normal concentration. Second, an aliquot of solvent was placed in a 200-mL triangle flask and was moved into a vibrating hot bath kept at the experimental temperature. After the solvent reached an experimental temperature, an aliquot of raw material (mixture oil), kept at the experimental temperature, was added into it. They were left for 48 hr, and then reached equilibrium.

Third, after stopping the vibration, the mixture was settled for an aliquot of time and the raffinate phase and the extract phase were split with a separatory funnel. The compositions of the raffinate phase and the extract phase resulting from the extraction were measured according to the abovementioned analysis for the distillate.

The material system and experimental conditions are summarized in Table 2. Each different equilibrium state could be obtained by varying the mass ratio of a solvent to a feed at initial $(S/F)_0$ [$(S/F)_0 = 0.5, 1, 2, 3$].

To confirm the time to reach equilibrium, the raffinate phases and the extract phases obtained through contacting (contact time: 12, 24, 36, 48 hr)

Table 2. System and experimental conditions for batch equilibrium extraction.

System	
Raw material	Distillate recovered from batch distillation of LCO + n-Decane
Solvent	Dimethylformamide (DMF) + Water
Conditions	
Contact time, t (hr)	48
Mass fraction of water in solvent at initial, $y_{w,0}$ (−)	0.02−0.1
Mass ratio of solvent to raw material at initial, $(S/F)_0$ (−)	0.5−3
Operation temperature, T (°C)	9−40

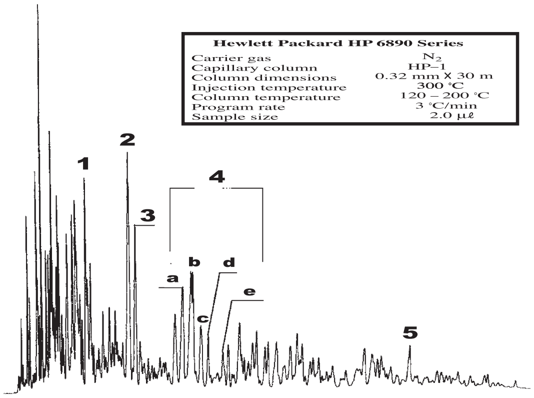
a solvent and a raw material under an identical conditions [operating temperature, $(S/F)_0$, mass fraction of water in solvent at initial] were analyzed. The compositions of the raffinate phases and the extract phases obtained through contact for 24, 36, and 48 hr were the same, irrespective of contact time.

RESULTS AND DISCUSSION

Gas Chromatogram and Composition of LCO

LCO[1,2] is composed of about 300 to 500 hydrocarbons. Approximately 80 wt% are aromatic components and the rest are paraffin components, which are carbon number 10–25. The aromatic components are monocyclic, bicyclic, and tricyclic aromatic components; monocyclic aromatic components were an alkylbenzene group and an indane group; bicyclic aromatic components a naphthalene group, a biphenyl group, and a fluorene group; and tricyclic components an anthracene group.

Figure 2 shows the gas chromatogram of LCO and the component names of hydrocarbons identified. Peak 1 presents naphthalene and peak 5 phenanthrene. It indicates that the LCO contained a significant amount of monocyclic and bicyclic aromatic components. Though DMNA of 10 structural isomers presented five peaks, they all were summed and regarded as one component. Table 3 shows the composition of the hydrocarbons quantified. LCO contained about 9 wt% of DMNAs and 2.3 wt% of a mixture of 2,6- and 2,7-DMNA isomers.



Legend
1: naphthalene (NA) 2: 2-methylnaphthalene (2-MNA) 3: 1-methylnaphthalene (1-MNA)
4: dimethylnaphthalene (DMNA) mixture with ten structural isomers (DMNAs)
  a: 2,6- and 2,7-DMNA mixture   b: 1,7-, 1,3- and 1,6-DMNA mixture
  c: 1,4-, 2,3- and 1,5-DMNA mixture   d: 1,2-DMNA
  e: 1,8-DMNA
5: phenanthrene (PNTR)

Figure 2. Gas chromatogram of LCO.

Distillation

Concentration of DMNA Isomers from LCO

In this work, the effect of reflux ratio (R) on the concentration of DMNAs by the batch distillation operation could not be measured, because the compositions of the distillates obtained through operating the distillation at R = 0.5, 1, and 2 were almost the same, irrespective of *R*.

Figure 3 shows the result that DMNAs were concentrated by the batch distillation at R = 0. Naphthalene (NA; bp: 217°C), 2-methylnaphthalene (2-MNA, bp: 242°C), and 1-methylnaphthalene (1-MNA, bp: 243°C), and DMNAs (bp: 262 to 271.44°C) showed a maximum concentration at V_f = 0.4 (distilled temperature = 219°C), at V_f = 0.5 (distilled temperature = 243°C), at V_f = 0.5 (distilled temperature = 243°C), and at V_f = 0.65 (distilled temperature = 266°C), respectively. The distilled temperature of the distillate containing the maximum concentration of each component was close to the boiling point of each component. From the overlap of the maximum concentration of 2-MNA and 1-MNA, we knew that the split between isomer components by the distillation operation was very difficult.

Table 3. Composition of LCO.

Component (fraction)	Composition (mass)
Naphthalene (NA)	0.015
2-Methylnaphthalene (2-MNA)	0.030
1-Methylnaphthalene (1-MNA)	0.018
Dimethylnaphthalene (DMNA) mixture with ten structural isomers (DMNAs)	0.091
2,6- and 2,7-DMNA mixture	0.023
1,7-, 1,3- and 1,6-DMNA mixture	0.040
1,4-, 2,3- and 1,5-DMNA mixture	0.013
1,2-DMNA	0.008
1,8-DMNA	0.007
Phenanthrene (PNTR)	0.005

Also, the distillate at $V_f = 0.65$ (distilled temperature = 266°C) contained little NA and phenanthrene (bp: 340°C) because the differences between the boiling points of NA or phenanthrene and DMNAs are higher than those of boiling points between 2-MNA or 1-MNA and DMNAs. Also, assuming that the vapor and the liquid are the ideal state, the values of relative

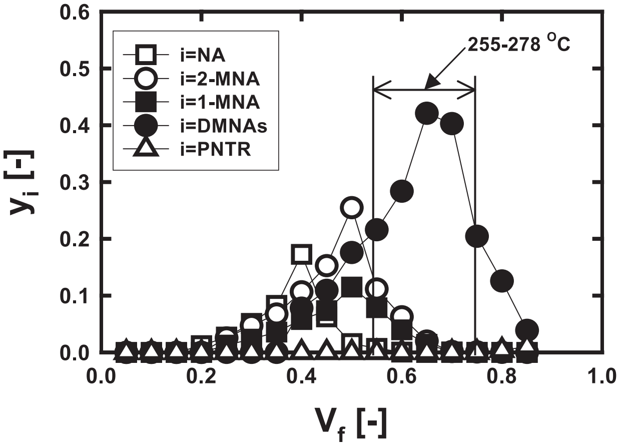
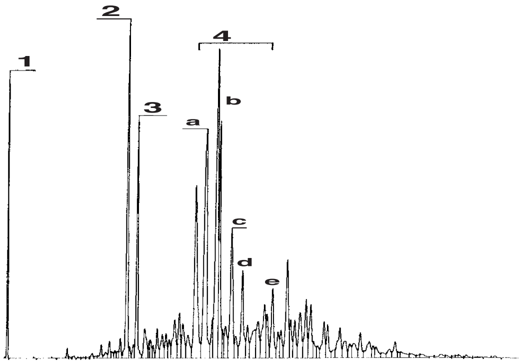


Figure 3. Relationship between mass fraction of each component in distillate and distilled ratio. Reflux ratio = 0, NA: naphthalene, 2-MNA: 2-methylnaphthalene, 1-MNA: 1-methylnaphthalene, DMNAs: dimethylnaphthalene mixture with ten structural isomers, and PNTR: phenanthrene.

volatilities of NA, 2-MNA, 1-MNA, and phenanthlene to DMNAs calculated from the Antoine equation at 266°C ($V_f = 0.65$) and 760 mm Hg are 2.6734, 1.6881, 1.565, and 0.1993, respectively. The boiling point range of DMNAs is 262 to 271.4°C. However, each distillate ($V_f = 0.55$ to 0.75) distilled at 255°C to 278°C, considering the recovery ratio (based on DMNAs mass in LCO) of DMNAs, was mixed. This distillate was used as a raw material for the extraction.

Gas Chromatogram and Composition of Distillate

Figure 4 shows the gas chromatogram and the component names of hydrocarbons identified for the mixture oil, which was added into a small quantity of DEC to the distillate ($V_f = 0.55$ to 0.75) recovered by the batch distillation. The composition of hydrocarbon components is summarized in Table 4. When the gas chromatogram of the distillate was compared with that of LCO (see Figure 2), there were only a few of the components appearing before 2-MNA and after phenanthrene. Subsequently, the peak of DMNAs considerably increased. DMNAs concentration of the distillate was found to be 30.63 wt%. This result indicated that the DMNAs concentration of the distillate was 3.4 times higher than that of LCO.



Legend
1: n-decane (DEC) 2: 2-methylnaphthalene (2-MNA) 3: 1-methylnaphthalene (1-MNA)
4: dimethylnaphthalene (DMNA) mixture with ten structural isomers (DMNAs)
a: 2,6- and 2,7-DMNA mixture b: 1,7-, 1,3- and 1,6-DMNA mixture
c: 1,4-, 2,3- and 1,5-DMNA mixture d: 1,2-DMNA e: 1,8-DMNA

Figure 4. Gas chromatogram of the mixture oil added a small quantity of n-decane to the distillate recovered at temperature range of 255°C to 278°C.

Table 4. Composition of the mixture oil added a small quantity of n-decane to the distillate* recovered by batch distillation of LCO.

Component (fraction)	Composition (mass)
n-Decane (DEC)	0.012
Naphthalene (NA)	0
2-Methylnaphthalene (2-MNA)	0.038
1-Methylnaphthalene (1-MNA)	0.026
Dimethylnaphthalene (DMNA) mixture with ten structural isomers (DMNAs)	0.303
2,6- and 2,7-DMNA mixture	0.094
1,7-, 1,3- and 1,6-DMNA mixture	0.117
1,4-, 2,3- and 1,5-DMNA mixture	0.041
1,2-DMNA	0.029
1,8-DMNA	0.022
Phenanthrene (PNTR)	0

*Temperature range of distillate recovered: 255°C to 278°C.

Concentration efficiency for DMNAs recovered by a batch distillation apparatus of this work was found to be low, because of the simple batch distillation unit for the separation of each component, the boiling point range of components of LCO near to that of DMNAs, and the recovery ratio for DMNAs. When LCO is distilled at optimal distillation conditions by multistage continuous distillation, it is expected that the separation performance will be much better than that of this work. Therefore, it seems that a continuous operation with multistage distillation column at optimal distillation conditions results in changing low concentration efficiency, which appeared through this work with high concentration efficiency.

Extraction

Definition Equation

The yield (Y_i) of component *i* was defined as Eq. 1.

$$Y_i = (Ey_i)/(R_0 x_{i,0}) \qquad (1)$$

where E and R_0, respectively, denote the mass of the extract phase and that of the raw material. $x_{i,0}$ and y_i, respectively, denote the mass fraction of component *i* in raw material and that in the extract phase.

Selectivity of component *i* based on component *j*, $\beta_{i,j}$, was defined as Eq. 2.

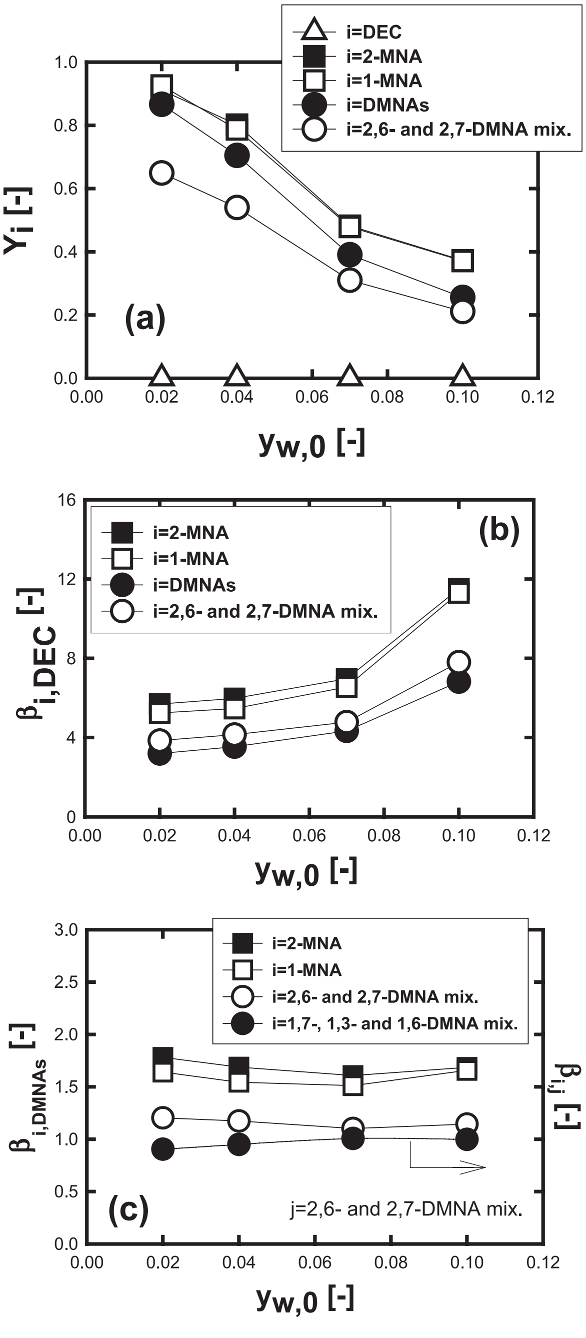
$$\beta_{i,j} = (y_i/x_i)/(y_j/x_j) \tag{2}$$

where y_i and y_j, respectively, denote the mass fraction of component *i* and component *j* in the extract phase, and x_i and x_j, respectively, the mass fractions of component *i* and component *j* in the raffinate phase.

Separation Between Aromatic and Paraffin Components in the Distillate

Figure 5(a) through (c) show the effect of the moisture content of solvent at initial ($y_{w,0}$) on the yield (Y_i) of component *i*, the selectivity of component *i* based on DEC ($\beta_{i,DEC}$), and the selectivity of component *i* based on DMNAs ($\beta_{i,DMNAs}$) [at $(S/F)_0 = 1$, $T = 25°C$]. The yields of each bicyclic aromatic component or the mixture were much higher than those of the paraffiin component (DEC), as shown in Figure 5(a). The yields of 2-MNA and 1-MNA (carbon number 11) were higher than those of DMNAs and the mixture of 2,6-DMNA and 2,7-DMNA (carbon number 12) due to the solubility of each component in the solvent. The yield increased with decreasing the carbon number of the aromatic component. In components with the same carbon number, the yields of 2-MNA and 1-MNA were almost the same. However, the yields of DMNAs were higher than that of the mixture of 2,6-DMNA and 2,7-DMNA. It was expected that the solubility of the mixture of 2,6-DMNA and 2,7-DMNA in aqueous DMF was less than that of the others (eight species of DMNA). Increasing $y_{w,0}$ resulted in decreasing the solubility of a hydrophobic component because the polarity of a solvent increased with increasing its moisture. Therefore, the yields of each hydrophobic bicyclic component decreased, accordingly, as $y_{w,0}$ increased. The yields of 2-MNA, 1-MNA, DMNAs, and the mixture of 2,6-DMNA and 2,7-DMNA at $y_{w,0} = 0.02$, respectively, were found to be 0.92, 0.91, 0.87, and 0.65. The yields of 2-MNA, 1-MNA, DMNAs. The mixture of 2,6-DMNA and 2,7-DMNA at $y_{w,0} = 0.1$, respectively, were found to be 0.38, 0.38, 0.26, and 0.21. These results indicated that increasing $y_{w,0}$ produced a sharp decrease in the yield. $\beta_{i,DEC}$ increased with increasing $y_{w,0}$, as shown in Figure 5(b). This phenomenon, also, indicated that the increase of $y_{w,0}$ produced a sharp increase of $\beta_{i,DEC}$ because the paraffin component (DEC) is much more hydrophobic than the bicyclic components.

The lower the carbon number of bicyclic aromatic component, the easier the separation between an aromatic group and a paraffin group. The


i=DEC
i=2-MNA
i=1-MNA
i=DMNAs
i=2,6- and 2,7-DMNA mix.
Y_i [-]
(a)
1.0
0.8
0.6
0.4
0.2
0.0
0.00
0.02
0.04
0.06
0.08
0.10
0.12
$y_{w,0}$ [-]
i=2-MNA
i=1-MNA
i=DMNAs
i=2,6- and 2,7-DMNA mix.
(b)
$\beta_{i,DEC}$ [-]
16
12
8
4
0
0.00
0.02
0.04
0.06
0.08
0.10
0.12
$y_{w,0}$ [-]
i=2-MNA
i=1-MNA
i=2,6- and 2,7-DMNA mix.
i=1,7-, 1,3- and 1,6-DMNA mix.
$\beta_{i,DMNAs}$ [-]
$\beta_{i,j}$ [-]
(c)
j=2,6- and 2,7-DMNA mix.
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.00
0.02
0.04
0.06
0.08
0.10
0.12
$y_{w,0}$ [-]

selectivities of 2-MNA, 1-MNA, DMNAs, and the mixture of 2,6-DMNA and 2,7-DMNA at $y_{w,0} = 0.02$, respectively, were found to be 5.8, 5.3, 4, and 3.4. The selectivities of 2-MNA, 1-MNA, DMNAs, and the mixture of 2,6-DMNA and 2,7-DMNA at $y_{w,0} = 0.1$, respectively, were found to be 11.7, 11.4, 7.8, and 7.0. These results indicated that increasing $y_{w,0}$ produced the increase of the selectivity. The higher the carbon number of the paraffin component, the lower the solubility of the paraffin component in the solvent.[26] In reality, the carbon number of the paraffin component in the raw material (distillate) for the extraction was 2 to 7 times higher than that of DEC. Therefore, even though any of the paraffin in the distillate was used as a reference component, it was expected that the selectivities were higher than those which used DEC as a reference. These results suggested that the selectivity of all aromatic components mixtures based on all the paraffin components mixture in the distillate could be very high. From Figure 5(c), it can be suggested that the larger the difference of the carbon number among the aromatic components, the easier the separation of each aromatic component. However, the selectivity between aromatic components with the same carbon number was almost 1, and it was difficult to separate each isomer component.

Figure 6(a) through (c) show the effect of the mass ratio of solvent/raw material at initial $(S/F)_0$ on Y_i, $\beta_{i,DEC}$, and $\beta_{i,DMNAs}$ (at $T = 25°C$, $y_{w,0} = 0.04$). Y_i increased with increasing $(S/F)_0$, as shown in Figure 6(a). The yields of 2-MNA, 1-MNA, DMNAs, and the mixture of 2,6-DMNA and 2,7-DMNA at $S/F = 0.5$, respectively, were found to be 0.30, 0.30, 0.23, and 0.25. The yields of 2-MNA, 1-MNA, DMNAs, and the mixture of 2,6-DMNA and 2,7-DMNA at $S/F = 3.0$, respectively, were found to be 0.99, 0.98, 0.88, and 0.73. In Figure 6(b), $\beta_{i,DEC}$ increased linearly with increasing $(S/F)_0$. This result indicated that the aromatic components could be easily separated from the paraffin components with increasing $(S/F)_0$. The selectivity of the aromatic component at $(S/F)_0 = 0.5$ was found to be almost 2.5, irrespective of component. The selectivities of 2-MNA, 1-MNA, DMNAs, and the mixture of 2,6-DMNA and 2,7-DMNA at $S/F = 3$ increased sharply and were found to be 17, 12, 9, and 8, respectively. From Figure 6(c), it can be suggested that the larger the difference of the carbon number among aromatic components or the higher the $(S/F)_0$, the easier the separation of each aromatic component, and it was difficult to separate each aromatic component with the same carbon number.

Figure 5. The effect of the moisture content of solvent at initial ($y_{w,0}$) on (a) the yield of component i, (b) the selectivity of component i based on DEC, and (c) the selectivity of component i based on DMNAs. $(S/F)_0 = 1$, $T = 25°C$.

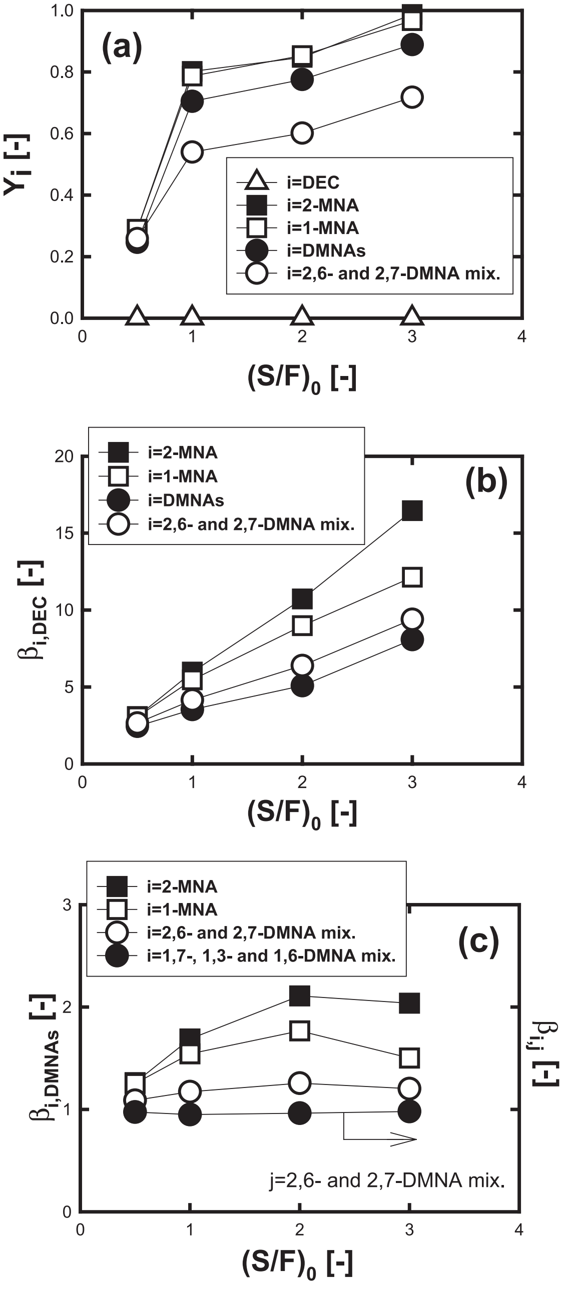


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Figure 7(a) through (c) show the effect of the operation temperature (T) on Y_i, $\beta_{i,DEC}$, and $\beta_{i,DMNAs}$ (at $y_{w,0} = 0.04$, $(S/F)_0 = 1$). The operation temperature had no effect on Y_i. As shown in Figure 7(b), increasing the operation temperature resulted in decreasing the selectivity of the aromatic components. The selectivities of 2-MNA, 1-MNA, DMNAs, and the mixture of 2,6-DMNA and 2,7-DMNA at T = 9°C, respectively, were found to be 7, 6.7, 3.9, and 4.7. At T = 40°C, respectively, they were found to be 3.7, 3.3, 2.5, and 2.7. From Figure 7(c), it can be suggested that the larger the difference of the carbon number among aromatic components and the lower the operation temperature, the easier the separation of each aromatic component. However, it was difficult to separate among aromatic components with the same carbon number.

When the extraction (at $y_{w,0} = 0.04$ and $(S/F)_0 = 1$) was carried out at above 40°C, two phases of the raffinate phase and the extract phase did not coexist. These results indicated that the DMF extraction of DMNAs in distillate could be operated even at room temperature.

From the above results for the effect of the extraction parameters on the yield of DMNAs and the selectivity of DMNAs based on the paraffin component (DEC), it was expected that when DMNAs in the distillate were extracted at $y_{w,0} = 0.1$, $(S/F)_0 = 3$, and T = room temperature by the multistage continuous extraction unit, a higher yield and selectivity were accomplished. Therefore, the extraction operation using aqueous DMF as the extraction solvent seemed to be optimal method for dearomatizing of the distillate.

The Gas Chromatogram of Raffinate and Extract Phase Without Solvent

Figure 8(a) and (b), respectively, show the gas chromatograms of the raffinate phase and the extract phase without a solvent resulting from extraction of the distillate including a small quantity of DEC [at $y_{w,0} = 0.1$, $(S/F)_0 = 3$, T = 25°C]. Figure 8(a) shows that the gas chromatogram (except peak 1 of DEC) of the raffinate phases was very different from that of the distillate recovered by the distillation of LCO (see Figure 4). The peaks of aromatic components (NA, 2-MNA, 1-MNA, and DMNAs) identified in this work could not be found because a large quantity of the aromatic components in the distillate were extracted with the extraction. The peaks

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Figure 6. The effect of the mass ratio of solvent/raw material at initial $[(S/F)_0]$ on (a) the yield of component i, (b) the selectivity of component i based on DEC, and (c) the selectivity of component i based on DMNAs. $y_{w,0} = 0.04$, T = 25°C.

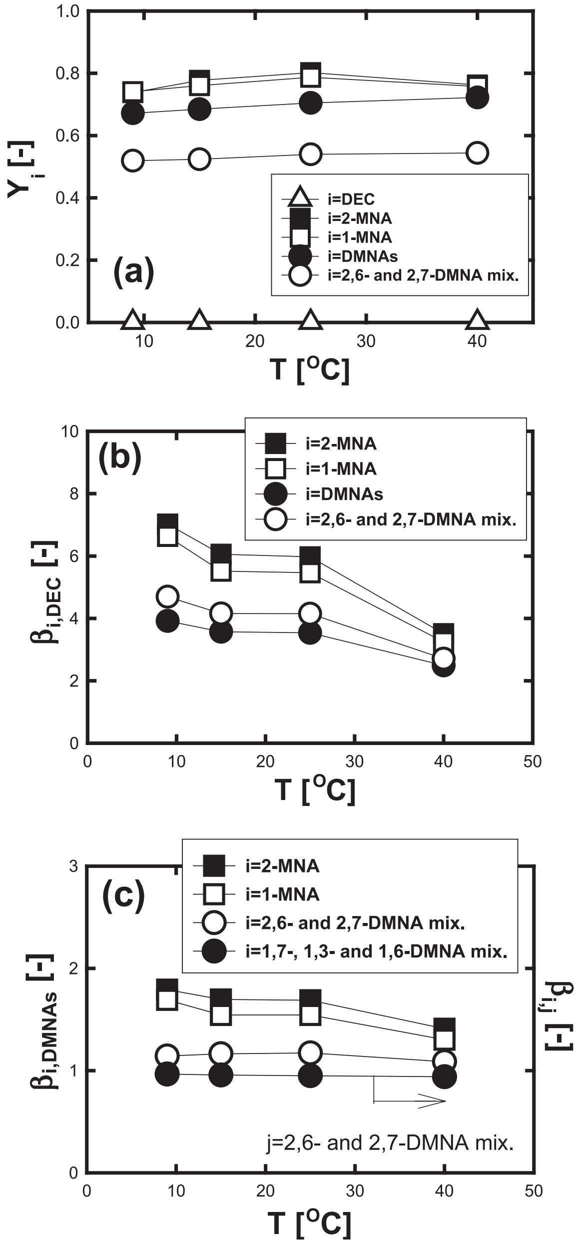
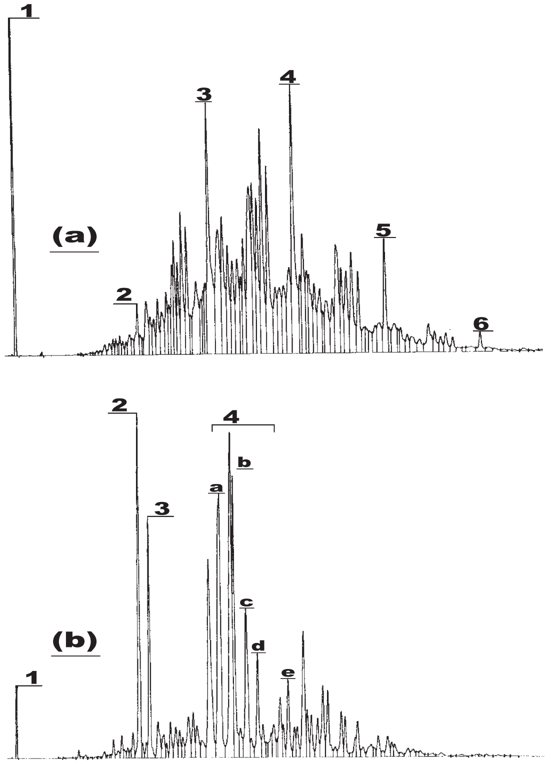


Figure 7. The effect of the operation temperature at initial (T) on (a) the yield of component i, (b) the selectivity of component i based on DEC, and (c) the selectivity of component i based on DMNAs. $y_{w,0} = 0.04$, $(S/F)_0 = 1$.



Legend

Gas chromatogram (a)

1: n-decane (DEC) 2: n-tridecane 3: n-tetradecane

4: n-pentadecane 5: n-hexadecane 6: n-heptadecane

Gas chromatogram (b)

1: n-decane (DEC) 2: 2-methylnaphthalene (2-MNA) 3: 1-methylnaphthalene (1-MNA)

4: dimethylnaphthalene (DMNA) mixture with ten structural isomers (DMNAs)

a: 2,6- and 2,7-DMNA mixture b: 1,7-,1,3- and 1,6-DMNA mixture

c: 1,4-, 2,3- and 1,5-DMNA mixture d: 1,2-DMNA e: 1,8-DMNA

Figure 8. Gas chromatogram of (a) the raffinate phase, and (b) the extract phase without a solvent. $y_{w,0} = 0.04$, $(S/F)_0 = 3$, and $T = 25°C$.

of the paraffin components with carbon numbers from 13 to 17 were considerably increased due to the increasing the concentration of the paraffin components in the raffinate phase. When the gas chromatogram of the extract phase (except peak 1 of DEC) in Figure 8(b) was compared with that of Figure 4, the peak heights of the aromatic components were increased. Also, from the difference of the peak height of DEC (peak 1) in

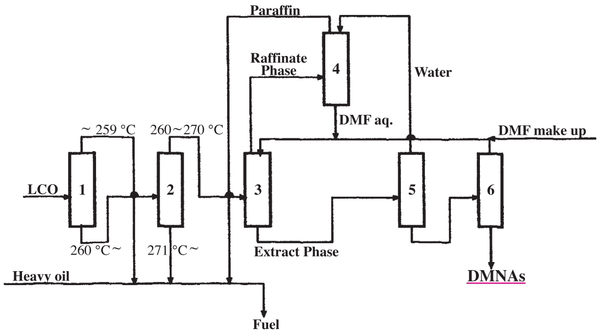


Figure 9. Separation and recovery process of dimethylnaphthalene isomers from LCO. Column 1, 2, 5, and 6: the distillation columns; column 3: the extraction column; and column 4: the washing column.

Figure 8(a) and (b), the effect of the extraction on the separation between the aromatic components and the paraffin components in the distillate could be reconfirmed.

Process for Recovery of DMNA Isomers from LCO

The process of the separation and recovery of DMNAs from LCO was investigated using the results obtained from the distillation and the extraction. As shown in Figure 9, the process suggested was composed of four distillation columns, one extraction column, and one washing column. Column 1 and 2 were the distillation columns for recovering the distillate including DMNAs of high concentration, column 3 the extraction column for separating between DMNAs and paraffin components in the distillate. Colum 4 was the washing column for recovering the paraffin components of the raffinate phase, and columns 5 and 6 were the distillation columns for recovering water and DMF respectively, in the solvent.

CONCLUSION

The separation and recovery of DMNA isomers in LCO was examined by a distillation-extraction combination. The following conclusions resulted from the present examination.

1. DMNA isomers of which 9 wt% in LCO were concentrated by the batch distillation, and the distillate with DMNA isomers of high

concentration as much as 30.63 wt% was recovered by mixing distillates distilled at 255–278°C.

2. An equilibrium extraction which investigated the separation between DMNA isomers and paraffin components in a distillate was carried out using an oil mixture added a small quantity of n-decane to the distillate recovered through the batch distillation as a raw material and the aqueous N,N-dimethylforamide as a solvent. Increasing the moisture content of the solvent and the mass ratio of solvent/raw material resulted in improving the separation between DMNA isomers and the paraffin components in the distillate, but increasing the operation temperature resulted in deteriorating the separation between DMNA isomers and the paraffin components in the distillate.
3. The process for the separation and recovery of DMNA isomers from LCO was investigated by using the results obtained from the distillation and the extraction. The suggested process was composed of the distillation column (two) for recovering the distillate including DMNA isomers of high concentration, the extraction column (one) for separating between the paraffin components and the aromatic components in the distillate, the washing column (one) for recovering the paraffin components in the raffinate phase, and the distillation column (two) for recovering, respectively, water and DMF in the solvent.

The process proposed by this work is a new one, considerating the separation between the paraffin components and the aromatic components in the distillate, also, and a simple one, without a re-extraction operation by using DMF as the extraction solvent of the distillate. Therefore, this proposed process would be a feasible process to recover DMNA isomers of LCO.

NOMENCLATURE

E	mass of extract (solvent) phase (Kg)
F	mass of raw material (kg)
R	mass of raffinate phase (Kg) or reflux ratio (–)
S	mass of solvent (kg)
T	operating temperature (°C)
t	contact time (s)
V_f	distilled ratio (distillate volume/raw material volume) (–)
x	mass fraction in raw material or raffinate phase (–)

Y	yield defined by Eq. 1 (−)
y	mass fraction in distillate or extract phase (−)

Greek

β	selectivity defined by Eq. 2 (−)

Subscript

DEC	n-decane
DMNAs	dimethylnaphthalene mixture with ten structural isomers
i	component *i*
j	component *j*
1-MNA	1-methylnaphthalene
2-MNA	2-methylnaphthalene
NA	naphthalene
W	city water
0	at initial (t = 0)

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